09/402674

514 Rec'd PCT/PTO 08 OCT 1999

Polyol and complex esters for use with, in particular, flu rinated refrigerants

The present invention concerns a refrigerant compositions according to the preambles of claims 1, 3, 5 and 7. Compositions of this kind generally contain a non-chlorinated hydrofluorocarbon based refrigerant composition together with a polyol ester based lubricant mixed therewith.

The invention also concerns complex esters according to claim 16 and the use thereof in lubricants.

Lately, as a result of development in many fields of application, the evolution of polyolester type lubricants has been rapid. These products can be used as such or mixed with another base oil, such as a hydrocarbon, in engine oils for automotives, in aeroplane and gas turbine oils, as biodegradable hydraulic oils, as metal working oils and as compressor oils. These products are used in particular together with fluorinated refrigerants as a soluble lubricant component in refrigeration compressors due to their advantageous solubility properties, good technical stability and good cold properties.

The use of, e.g., neopentylglycol and pentaerytritol esters together with refrigerants has been generally suggested. Although these known esters in principle exhibit good lubricant properties, their solubility in non-chlorinated hydrofluorocarbons is often only fair. For this reason they do not work well enough in refrigerant compositions containing fluorinated hydrocarbons.

It is an object of the present invention to eliminate the problems of the prior art and to provide polyol and complex esters of a novel kind which can be used in particular together with fluorinated refrigerant liquids as lubricants. It is another object of the invention to provide novel esters which are generally suited to the use as base oils of lubricants.

The present invention is based on the finding that polyol or complex esters of 3-hydroxy-2,2-methyl-3-hydroxy-2,2-dimethylpropionate, i.e. hydroxypivalyl hydroxypivalate, which have good lubricant properties, also exhibit a good or excellent solubility in fluorinated refrigerants and they are therefore suitable for use in refrigerant compositions containing this kind of refrigerants. In particular the polyol esters used comprise the polyol HPHP (hydroxypivalyl hydroxypivalate) as such or together with another polyol, such as NPG, BEPD, ETHD, TMP, TME or PE and the carboxylic acid is a linear or branched C_5 - C_{18}

monocarboxylic acid or a hydroxy acid, such as hydroxypivalic acid or a mixture of mono- and dicarboxylic acids, such as adipic acid, sebasic acid, azelaic acid, dimethylmalonic acid or cyclic anhydrides.

More specifically, the refrigerant composition according to the present invention is mainly characterized by what is stated in the characterizing parts of claims 1, 3, 5 and 7.

Complex esters of HPHP are novel and useful as base oils of lubricant oils. The novel esters are characterized by what is stated in the characterizing part of claim 16.

The present invention provides considerable advantages. Thus, as mentioned above, the esters of HPHP have good lubricant properties and good solubility in HFC compounds used as refrigerants. The raw materials of said oils can be produced by the economically advantageous oxo-process (hydroformulation). The properties of the oils can easily be modified depending on the application by varying the ratio of the polyols of the ester (the amount of HPHP can be 100 to 5 mol-% of the total amount of polyol), the esterifying carboxylic acid and/or the ratio between the esterifying carboxylic acids. By using branched acids the solubility can be improved and by using dibasic acids the viscosity can be raised.

In the following, the invention will be examined with the aid of a detailed description and using a number of working examples.

The present esters comprise polyol or complex esters of 3-hydroxy-2,2-~~methyl~~ dimethylpropyl 3-hydroxy-2,2-dimethylpropionate. "Polyol ester" means i.a. esters having a carboxylic group comprising a monobasic acid or an anhydride thereof. For the purpose of the present invention, the term "polyol ester" comprises generally also "complex esters" which are esters in which at least a part of the esterifying acids are dibasic. Usually both carboxylic groups of these acids react with an alcohol and yield oligomeric ester compounds, which contain at least two alkohol residues and one carboxylic acid residue. Complex esters also include esters having the carboxylic acid residue formed by a hydroxy acid containing both a hydroxyl group and a carboxylic group. The carboxylic group reacts with the polyol, whereas the hydroxyl group reacts with the carboxylic group of another carboxylic acid. NE 3.26.01

"Polyol" stands for a compound with at least two hydroxy groups. According to the present invention HPHP can be esterified alone or together with another polyol. These polyols are,

e.g., NPG (neopentylglycol), BEPD (2-butyl-2-ethyl-1,3-propanediol), ETHD (2-ethyl-1,3-hexanediol), TMP (trimethylol propane), TME (trimethylol ethane), PE (pentaerythritol), TMPD (2,2,4-trimethyl-pentanediol) and CHDM (1,4-dimetylol-cyclohexane). Of these polyols chemically and technically stable polyols, containing no hydrogen in the carbon in position 2 or which are (sterically) strongly hindered, such as NPG, ETHD, CHDM and BEPD, are particularly preferred.

Preferably the polyol ester mixtures are formed by mixing the polyols together and by esterifying the thus formed mixture *in situ*.

According to a first preferred embodiment of the invention, a refrigerant composition is provided, comprising a polyol ester which completely or almost completely (95 mol-%, or even 100 %) consists of an ester of HPHP.

According to a second preferred embodiment of the present invention, a refrigerant composition is provided, comprising in addition to a polyol ester of HPHP an ester of TMP, TME, PE or TMPD at any ratio. Preferably HPHP forms the main part of the polyol residue of the ester mixture, i.e. its molar amount is 50 % - 100 %.

According to a third preferred embodiment of the present invention, a refrigerant composition is provided, comprising in addition to a polyol ester of HPHP a polyol ester of BEPD, the molar ratio between BEPD and HPHP being 5:95 to 99:1.

According to a fourth preferred embodiment of the present invention, a refrigerant composition is provided, comprising in addition to a polyol ester of HPHP a polyol ester of NPG, ETHD or CHDM.

HPHP or a mixture of HPHP and some other polyol is esterified with a linear or branched C_4 to C_{18} carboxylic acid or an anhydride thereof. As specific examples of aliphatic, linear or branched, saturated or unsaturated C_4-C_{18}-carboxylic acids which can be used for preparing the ester, the following can be mentioned:

I saturated, linear C_4-C_{18}-carboxylic acids: butanoic acid (butyric acid), pentanoic acid (valeric acid), hexanoic acid (caproic acid), heptanoic acid, octanoic acid (caprylic acid), decanoic acid (capric acid), dodecanoic acid (lauric acid) and hexadecanoic acid (palmitic acid) and mixtures thereof;

II saturated, branched C_4-C_{16}-carboxylic acids: isobutanoic acid, 2-ethylhexanoic acid, isononanoic acid and 3,5,5-trimethylhexanoic acid;

III unsaturated, linear C_4-C_{18}-carboxylic acids: 3-butenoic acid (vinylacetic acid); and

IV unsaturated, branched C_4-C_{18}-carboxylic acids.

In the mixed esters the ratios between the various linear and branched carboxylic acids can vary within large boundaries. Typically, the linear carboxylic acid(s) is (are) present in amounts of 1 to 100 mol-%, preferably about 10 to 90 mol-% of the amount of carboxylic acids. Correspondingly, the amount of branched carboxylic acids is 99 to 1 mol-%, preferably about 90 to 10 mol-%. In particular it is possible to prepare polyolesters, which contain 10 to 50 mol-% of at least one linear carboxylic acid and 90 to 50 mol-% of a branched carboxylic acid.

When polyol esters of HPHP are prepared it is preferred to select linear or branched acids containing 4 to 14 carbon atoms as esterifying carboxylic acid. Octanoic acid, 2-ethylhexanoic acid and lauric acid can be mentioned as examples.

Esterifying hydroxy acids are, e.g., hydroxypivalic acid (HPAA), lactic acid, citric acid and dimethylolpropionic acid (DMPA).

In addition to the afore-mentioned, the esterifying carboxylic acid used can comprise dibasic carboxylic acids, such as oxalic acid, malonic acid, dimethylmalonic acid, succinic acid, glutaric acid, adipic acid, sebacic acid, pimelic acid, suberic acid and azelaic acid. It is also possible to use cyclic anhydrides, such as succinic anhydride or alkyl derivaties thereof, or trimellitic anhydride. Small amounts of aromatic anhydrides, such as phthalic anhydride are also possible.

The degree of esterification of the polyols is 50 to 100 %, preferably as high as possible, at least about 90 %. In the complex esters the ratio between the mono- and dibasic carboxylic acids is 50 : 50 to 99 : 1.

The polyol esters/mixed esters/complex esters of HPHP or HPHP and at least another polyol can be used for preparing refrigerant compositions. These contain as a refrigerant one or several chlorine-free hydrofluorocarbon(s) (a refrigerant) in which the ester is dissolved. As specific examples of the refrigerant liquid component of the compositions, the following can be mentioned: hydrofluorocarbon 134 (1,1,2,2-tetrafluoroethane),

hydrofluorocarbon 134a, hydrofluorocarbon 143 (1,1,2-trifluoroethane), hydrofluorocarbon 143a (1,1,1-trifluoroethane), hydrofluorocarbon 152 (1,2-difluoroethane) and hydrofluorocarbon 152a (1,1-difluoroethane). Of these compounds, hydrofluorocarbon 134a is generally preferred. Mixtures of hydrofluorocarbons can also be employed. Examples include hydrofluorocarbon mixture 407 (mixture of hydrocarbons 32, 125 and 134a) and hydrofluorocarbon mixture 410 (mixture of hydrocarbon 32 and 125).

Depending on application, the viscosity requirement for the ester is, according to ISO-standard, between 5 and 200 cSt (40 °C). Low (5 - 10) and intermediate (22 - 32) viscosities are needed for, e.g., refrigerators and other small refrigeration devices. High viscosity (46 - 68) compositions are used for, e.g., cooling equipment of air conditioners.

As already mentioned in the beginning, the viscosity of the prepared esters can be adjusted as desired by suitably selecting esterifying carboxylic acid components and/or by adding a further polyol to the BEPD. Thus, by using conventional linear or branched carboxylic acids (C_4 - C_{12}) and, e.g., adipic acid, it is possible to prepare esters having viscosities in the range of about 15-22 cSt at 40 °C. Their viscosity indeces are about 100 and pour points below −40 °C. They are suitable for use in smallish cooling equipment. By increasing the amount of a branched carboxylic acid it is possible to increase the solubility of the esters. By feeding a dibasic carboxylic acid into the esterification reaction and in particular by using it together with linear or branched acids, the viscosity of the product can be increased. The cold properties and good solubility remain. Mixing HPHP with another polyol before esterification makes it possible to increase even further without impairing the solubility . The viscosity increase to the range of high viscosity.

As examples of particularly valuable esters, the following can be mentioned:

I Polyol esters of HPHP, which contain 30 to 60 % linear carboxylic acid and 70 to 40 mol-% branched carboxylic acid

II Complex esters of HPHP which contain 1 to 10 mol-% dibasic carboxylic acid and 90 to 99 mol-% linear and/or branched monobasic carboxylic acid; and

III Complex esters of HPHP and NPG/BEPD, which contain 4 to 30 mol-% dibasic carboxylic acid and 96 to 70 mol-% linear and/or branched monobasic carboxylic acid.

As mentioned above, the complex esters of HPHP as well as complex esters of HPHP and

some other polyol, are already as such novel products which can be used in lubricant compositions for different aims. The esters work as base oil of these compositions and additives are usually employed in amounts of 0 to 20 wt.-% in the compositions for the purpose of modifying the compositions such that they are better suited for various applications. Thus, the esters are suitable not only for use in refrigerant compositions but also for all applications mentioned in the introduction of the specification.

Conventional additives which can be used in the refrigerant liquid compositions include, e.g., the following: antioxidants, antiwear agents, detergents, defoaming agents and corrosion inhibitors.

Suitable antioxidants include phenols, such as 2,6-di-t-butyl-4-methylphenol and 4,4'-methylene-bis(2,6-di-t-butylphenol); aromatic amines, such as p,p-dioctylphenylamine, monooctyldiphenylamine, phenothiazine, 3,7-dioctylphenothiazine, phenyl-1-naphthylamine, phenyl-2-naphthylamine, alkylphenyl-1-naphthatalamines and alkyl-phenyl-2-naphthal-amines, as well as sulphur-containing compounds, e.g. dithiophosphates, phosphitest, sulphides and dithio metal salts, such as benzothiazole, tin-dialkyldithiophosphates and zinc diaryldithiophosphates.

Suitable antiwear agents include, for example, phosphates, phosphate esters, phosphites, thiophosphites, e.g. zinc dialkyl dithiophosphates, zinc diaryldithiophosphates, tricresyl phosphates, chlorinated waxes, sulphurised fats and olefins, such as thiodipropionic esters, dialkyl sulphides, dialkyl polysulphides, alkyl-mercaptanes, dibenzothiophenes and 2,2'-dithiobis(benzothiazole); organic lead compounds, fatty acids, molybdenum complexes, such as molybdenum disulphide, halogen substituted organosilicon compounds, organic silicon compounds, borates and halogen-substituted phosphorus compounds.

As specific examples of suitable detergents, the following should be mentioned: sulphonates, aromatic sulphonic acids, which are substituted with alkyl having a long chain, phosphonates, thiophosphonates, phonolates, metal salts of alkylphenols, and alkyl sulphides.

Typical defoaming agents include silicon oils, e.g. dimethylpolysilozane and organic silicon compounds such as diethyl silicates.

Organic acids, amines, phosphates, alcohols, sulphonates and phosphites are examples of

corrosion inhibitors.

The esters according to the invention are prepared by a conventional esterification reaction wherein a polyol or a mixture of polyols is (are) reacted with an acid mixture in the presence of a catalyst or without a catalyst. Various acids, such as sulphuric acid, hydrochloric acid, p-toluene sulphonic acid, butyl titanate, tinoxide etc., are suitable catalysts for carrying out the invention. A particularly advantageous catalyst is tinoxide.

During the reaction, the polyol is reacted with the acid component by using an equivalent amount of acid, a deficient amount of acid or a surplus of acid; the excess acid amounts to typically a maximum of 10 mol-%, preferably about 0.1 to 5 mol-%, in particular about 1 mol-%. The reaction temperature is 150 to 230 °C, preferably 170 to 220 °C and in particular about 190 to 210 °C.

The esterification can be carried out as a batch or semibatch process for example by adding the remaining acid later on. The most typical embodiment comprises carrying out esterification in the melt phase but it is also possible to use a hydrocarbon-type medium, such as toluene or xylene. The product is neutralized either with conventional bases ($NaOH$, $NaHCO_3$, Na_2CO_3 etc.) or with organic amines and are then washed. The degree of purification of the ester product is preferably over 85 %, in particular over 90 % and the acid number of the ester is preferably below 0.1 mg KOH/g.

The following examples illustrate the invention. They do not, however, limit the scope of the invention.

Example 1
Determination of ester solubility

Solubility in fluorinated hydrocarbons was determined as follows: 1 ml of the studied ester was put into a test tube which was closed with a stopper. The test tube was placed in a cold bath at a temperature of −30 °C. When the temperature of the test tube and the ester had reached −30 °C (after about 5 minutes), a fluorinated refrigerant, such as R-134a, was added to make a total volume of 10 ml.

The ester-refrigerant mixture was allowed to stand in the bath at −30 °C with possibly a light occasional stirring. After about 15 minutes the mixture was visually assessed and it

was determined whether the mixture contained one or two phases. If the ester and the refrigerant liquid formed one phase, the ester is completely dissolved in the refrigerant liquid. If there are two phases present in the mixture, the ester is either partially or completely insoluble in the refrigerant liquid.

Example 2

Preparation of esters of HPHP

The preparation of esters of HPHP is described in the following using the esters of HPHP and heptanoic acid as an example.

The raw materials were weighed into a glass bulb according to the following recipe: HPHP 50 g and heptanoic acid 64.6 g. The catalyst used comprised 0.17 g tinoxide. The esterification was carried out by stirring using a mixer with an electric motor and by nitrigating the reaction mixture at about 210 °C. The reaction was complete wihin 7 hours.

Tinoxide was removed by filtration. Excess acid was neutralized from the reaction mixture with 2 - 5 wt-% triethylamine. The neutralization was carried out at 80 °C for 3 hours. Warm water (2 - 5 wt-%) was added to the reaction mixture and it was mixed cautiously. The solvent of the reaction mixture comprised heptane. Any formed aminocarboxylic acid salt or complex was separated. The solvent and the unreacted triethylamine were removed by vacuum distillation. The end product was filtered. The results are summarized in Table 1.

Table 1. Polyol esters of HPHP

Sample	Polyol	Acids (mol-%)	V_{40}	V_{100}	VI	PP(°C)	Solubility in R-134a	
							−30 °C	−50 °C
1	HPHP	Heptanoic acid (100)	11.63	2.98	111	-	Excellent	Excellent

Example 3

Preparation of esters of HPHP from acyclic anhydrides

The preparation of esters of HPHP is illustrated by using the preparation of an ester of HPHP and isobutyric anhydride as an example.

The raw materials were weighed into a glass reactor according to the following recipe: HPHP 17.5 g and isobutyric anhydride 19.36 g. The catalyst used comprised 0.37 g methanesulphonic acid. The esterification was carried out by adding the anhydride and the catalyst from a dropping funnel to the HPHP during 2 hours, and then the reaction mixture was stirred at about 150 °C for 2 hours.

Excess acid was neutralized from the reaction mixture and the catalyst was washed in a separation funnel with 3 x 25 ml 5 % sodium carbonate solution and 3 x 25 ml water. Any sodium salt or complex of the carboxylic acid were separated. Finally, the product was dried on sodium sulphate and filtered. Other esters were prepared by suitable modification of the conditions. The results are summarized in Table 2.

Table 2. Acid anhydride esters of HPHP

Sample	Polyol	Acids (mol-%)	V_{40}	V_{100}	VI	Solubility in R-134a	
						−30 °C	−50 °C
2	HPHP	Isobutyric anhydride	7.44	2.14	82	Excellent	
3	HPHP	2-ethylbutanoic anhydride	11.84	2.79	64	Excellent	Excellent

Example 4

Preparation of complex esters of HPHP

Complex esters of HPHP is described using the ester of HPHP, octanoic acid and adipic ester as an example.

The raw materials were weighed into a glass reactor according to the following recipe: HPHP 100 g, octanoic acid 94.8 g and adipic acid 24.0 g. The catalyst used comprised

0.328 g tinoxide. acid. The esterification was carried out by stirring and nitrigating the reaction mixture at about 210 °C. The reaction was complete within 7 hours.

Excess acid was neutralized from the reaction mixture with 5 wt-% triethylamine. The neutralization was carried out at 80 °C for 3 hours. Warm water (5 wt-%) was added to the reaction mixture and it was mixed cautiously. Any formed aminocarboxylic acid salt or complex was separated. The reaction mixture was then washed with a dilute mineral acid (1 molar H_3PO_4) and subsequently 1 to 2 times with warm water. Finally, the product was dried on sodium sulphate and filtered. Other esters were prepared by suitable modification of the conditions. The results are summarized in Table 3.

Table 3. Complex esters of HPHP

Sample	Polyol	Acids (mol-%)	V_{40}	V_{100}	VI	PP(°C)	Solubility in R-134a	
							−30 °C	−50 °C
4	HPHP	C_8 (80) AA (20)	39.8	7.06	140	-51	Good	
5	HPHP	C_8 (80) SA (20)	50.5	8.75	154	-51	Excellent	Excellent

A_A = adipic acid SA = sebasic acid C_8 = octanoic acid

Example 5

Preparation of polyol/complex esters of HPHP

Following the process of Example 4 complex esters of mixtures of HPHP and some other polyols were prepared. The results are indicated in Table 4.

Table 4. Polyol/c mplex esters of HPHP

Sample	Polyol	Acids (mol-%)	V_{40}	V_{100}	VI	PP(°C)	Solubility in R-134a	
							−30 °C	−50 °C
6	HPHP (60) BEPD (40)	C_8 (90) AA (10)	19.78	4.32	128	-63	Fair	
7	HPHP (60) BEPD (40)	C_8 (80) AA (20)	33.20	6.15	136	-54	Good	
8	HPHP (90) BEPD (10)	C_8 (90) AA (10)	21.57	4.61	133	-60	Excellent	Excellent
9	HPHP (60) NPG (40)	C_8 (80) AA (20)	23.69	5.06	147	-63	Excellent	
10	HPHP (90) BEPD (10)	C_8 (80) AA (20)	32.83	6.14	137	-60	Excellent	

BEPD = 2-butyl-2-ethyl-1,3-propanediol, NPG = neopentylglycol